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ning of each regular issue of the PCT Gazette.

(54) Title: CHEMICAL COMPOSITIONS AND METHODS FOR ABSORBING WATER VAPOUR AND COMBATING MAL-
ODOUR WITHIN A CAVITY

(57) Abstract: The invention relates to a method of absorbing water vapour and malodour from a cavity, for example a drawer or
wardrobe or the inside of a shoe. This is achieved by placement in the cavity of a package permeable to water vapour and retaining a
particulate dehumidifying compound, a particulate odour-combating compound, and a filler comprising starch or a starch derivative
or cellulose or a cellulose derivative, or which acts as a thickener or gelling agent for the water inside the package.

WO 03/063918 A1

Chemical Compositions and Methods for Absorbing Water
Vapour and Combating Malodour within a Cavity

This invention relates to the use of dehumidifying
5 compositions in absorbing water vapour and malodour from
the interior of cavities, for example wardrobes,
cupboards, drawers and shoes.

It is known to provide odour absorbing and/or sterilizing
10 compositions for use in combating odour produced by
domestic waste and by bodily fluids. In particular,
domestic waste placed in bins and waste receptacles can
generate significant malodour if left for any period of
time, especially when the waste is organic such as food
15 and beverage waste. Part of the malodour may be formed by
gaseous compounds released from the waste material, and
part of the malodour may be formed by volatile compounds
within moisture present in the waste material.

20 Various odour controlling agents have been disclosed in
the literature. Many odour-control materials have been
described for use with sanitary articles such as nappies
and feminine hygiene bins. US5885263 discloses
compositions comprising super absorbent polymers
25 containing boron species, which absorb moisture from waste
material in the vicinity of the odour controlling
composition. WO 01/52912 discloses absorbent articles,
such as sanitary napkins, panty liners and nappies
comprising lactic acid producing micro-organisms and odour
30 controlling zeolite compounds which absorb malodours from
waste material. WO 91/11977 discloses the use of zeolites
having intermediate $\text{SiO}_2/\text{AlO}_2$ ratios to control odours in
sanitary articles such as nappies and panty liners.

The odour-control compositions disclosed in the prior art discussed hereinabove comprise a malodour absorbing agent in conjunction with a moisture absorbing agent of a type
5 which absorbs water from moist material with which it is in contact.

It would be advantageous to provide a composition which absorbs malodour and water vapour, from a cavity.

10

According to a first aspect of the present invention there is provided a method of absorbing water vapour and of combating malodour within a cavity, the method comprising the step of introducing into the cavity a package
15 comprising a wall material which retains particulate contents and is permeable to water vapour, the contents comprising a dehumidifying compound, an odour-combating compound and a filler comprising starch or a starch derivative or cellulose or a cellulose derivative.

20

According to a second aspect of the present invention there is provided a method of absorbing water vapour and of combating malodour within a cavity, the method comprising the step of introducing into the cavity a
25 package comprising a wall material which retains particulate contents and is permeable to water vapour, the contents comprising a dehumidifying compound, an odour-combating compound, and a filler which acts as a thickener or gelling agent for the water inside the package.

30

The term "contents" is used throughout this specification to denote the mixture of the dehumidifying compound and

the odour-combating compound, and any other materials, mixed therewith, within the package.

Suitably the dehumidifying compound is capable of
5 absorbing at least its own weight of water vapour. Preferably it is capable of absorbing at least twice its own weight of water vapour. The package is preferably manufactured with the dehumidifying compound in a desiccated condition. Preferably the package is kept in a
10 dry environment between manufacture and sale. For example it may be wrapped in a wrapping which is impermeable to water vapour.

The dehumidifying compound is preferably a compound with a
15 high capacity to absorb water vapour. Its capacity to absorb standing water and water entrained in waste materials is not of significance, in this invention.

Preferably the dehumidifying compound comprises an
20 inorganic compound, for example calcium chloride and/or magnesium chloride. When calcium chloride is employed it preferably comprises less than 20wt% of the total contents. A preferred further dehumidifying compound, additional to calcium chloride, when needed, is magnesium
25 chloride.

Suitably the dehumidifying compound is present in an amount of at least 10wt%, preferably at least 20wt%, and most preferably at least 40wt%, of the weight of the dry
30 (total) contents. Suitably the dehumidifying compound is present in an amount of no more than 95wt%, preferably not more than 85wt% and most preferably not more than 75wt%, of the weight of the dry (total) contents.

The term "odour-combating" in this specification refers to any manner in which odour is counteracted by way of a physical or chemical action, for example by absorption, suppression, neutralisation or degradation; not merely odour-masking, as a fragrance alone may achieve.

Suitable odour-combating compounds include zeolites, inorganic carbonates, clays, for example bentonite, cyclodextrins and diatomaceous earths.

Suitably the odour-combating compound is present in an amount of at least 0.1wt% of the weight of the dry (total) contents, more preferably at least 0.5wt%, most preferably at least 1wt%. Suitably the odour-combating compound is present in an amount of no more than 25wt%, preferably no more than 20wt%, and most preferably no more than 10wt% of the weight of the dry (total) contents.

Preferably the odour-combating compound is a zeolite, most preferably comprised within a flowable zeolitic powder.

Preferably a flowable zeolitic powder comprises at least 80wt% zeolite, and preferably at least 90wt% zeolite. It may in certain useful embodiments be constituted substantially entirely by zeolite. When it is not, it may be zeolite admixed with a filler or, preferably, processing aid.

In this specification references to "zeolite" are to substantially virgin zeolite, including bound water of crystallisation and any atmospherically absorbed unbound water that may be present, but not including deliberately

added materials. "Zeolitic powder" denotes zeolite (as just defined) and also such a material containing deliberately added material(s).

5 Definitions which refer to the weight or weight ratio of zeolitic powder are made with reference to the zeolite (as defined above) in the zeolitic powder, unless otherwise stated.

10 We believe that the invention can be applied using any type of odour-absorbing zeolite or zeolitic powder, including odour-absorbing grades of the materials known as zeolite MAP, zeolite X, zeolite P and, most preferably zeolite A.

15

Suitably, the contents comprise a filler (additional to any starch, starch derivative, cellulose or cellulose derivative filler).

20 By "filler" we mean a compound which serves to increase the bulk of the composition and which, preferably, is substantially water insoluble. It may however have other functions - for example it may be a processing aid, and/or an odour-absorber and/or have water-absorbing properties
25 and/or act as a thickener or gelling agent for the water absorbed within the package.

A filler may be an inorganic filler, for example a metal salt or metal oxide.

30

A filler may be an organic filler, for example a compound in the cellulose or starch families (as mentioned above in defining the first aspect of the invention).

Suitable fillers include, for example, calcium carbonate, sodium bicarbonate, cellulose or cellulose derivatives, starch or starch derivatives, anhydrous calcium sulphate, calcium oxide, silica gel, and bentonite clays.

An especially preferred inorganic filler is one selected from the alkaline compounds able to neutralise foot acids, such as the Group IA and Group IIA carbonates and bicarbonates, for example, sodium bicarbonate, potassium bicarbonate, calcium carbonate and magnesium carbonate. Sodium bicarbonate is especially preferred.

An especially preferred organic filler is starch.

Suitably a filler (made up of one or more compounds) is present in an amount of at least 10wt%, preferably at least 20wt%, of the weight of the dry (total) contents.

Suitably a filler (made up of one or more compounds) is present in an amount of no more than 80wt%, preferably no more than 60wt%, more preferably no more than 40wt%, of the weight of the dry (total) contents.

As noted above some compounds which are primarily present as a filler may have odour-combating properties. Suitable fillers which have odour-combating properties include inorganic carbonates such as calcium carbonate, clays such as bentonite clays and silica gel.

However, preferred compositions comprise both a highly effective odour-combating compound and a separate filler which may or may not also absorb some odour.

According to this invention a filler which comprises starch or cellulose or a derivative thereof, or a filler which acts as a thickening or gelling agent, is an essential feature. Beyond that, even though some fillers also have some odour-combating properties (or other beneficial secondary properties), in this invention a filler is used in conjunction with a separate odour-combating compound, and is intended primarily as a bulking material, and thus is not an "odour-combating compound" according to the invention.

Preferred contents of the invention comprise a compound capable of absorbing at least its own weight of moisture, especially a magnesium or calcium halide, a filler, especially starch, and an odour-combating compound, especially a zeolite.

The contents may further comprise a fragrance. Many suitable fragrances are commercially available, including those designed to mask waste odours, and the choice of fragrance is a matter of subjective choice. If wished a fragrance may be entrained on an absorbent material, for example on a zeolite employed as an odour-absorbing compound, in order to give slow fragrance release.

The contents may suitably be in the form of a powder, or, preferably, granules (including flakes).

The cavity mentioned above may be an enclosed cavity, for example a drawer, wardrobe, cupboard, locker, refrigerator, freezer, cool box, car boot or car passenger

compartment. Preferably it is a drawer, wardrobe, cupboard or locker.

The cavity may be a non-enclosed cavity, for example the
5 inside of a shoe or boot.

In the method the package is placed inside the cavity and, if the cavity has a closure, it is typically closed. The package acts to reduce the humidity of the air inside the
10 cavity and prevent the development of musty odours.

The package may have a wall material which is all of semi-permeable (by which we mean permeable to water vapour and impermeable to water, that is, liquid water) membrane
15 material or may comprise a portion which is wholly water-impermeable membrane and a portion which is of semi-permeable membrane material.

In one convenient embodiment the package comprises a
20 sachet made up of two sheets joined together around their periphery, for example by heat sealing. Preferably one sheet is of a wholly water-impermeable membrane and the other sheet is of a semi-permeable membrane material.

25 Suitable technology for the package manufacture is described in US 6217701 and US 5935304.

Preferably the package is such that it can admit at least 500g, more preferably at least 1000g, most preferably at
30 least 2000g water vapour/m²/day.

The package may have a means for indicating exhaustion. For example the contents may include a component whose

colour changes when the water held by the contents reaches a certain level, indicative of exhaustion or imminent exhaustion. Alternatively the package may be designed to bulge visibly when replacement is needed (whilst being
5 designed to be safe from bursting) or otherwise to be detectable by feel, the contents becoming gel-like when approaching exhaustion. Alternatively the package may be formulated such when replacement is required water is no longer all retained by the contents but some drips
10 therefrom, and collects in a visible, distinct under-zone of the package. In that under-zone it may dissolve a colorant, to aid visual detection, or trigger another type of signal, for example a visible or audible signal.

15 In accordance with a further aspect of the present invention there is provided a package comprising a wall material which retains particulate contents and is permeable to water vapour, the contents comprising a dehumidifying compound, an odour-combating compound, and a
20 filler comprising starch or a starch derivative or cellulose or a cellulose derivative in admixture.

Alternatively, and according to a further aspect of the present invention there is provided a package comprising a
25 wall material which retains particulate contents and is permeable to water vapour, the contents comprising a dehumidifying compound, an odour-combating compound, and a filler which acts as a thickener or gelling agent for the water inside the package, in admixture.

30

The package is suitably in the form of a pouch or sachet. For certain embodiments it may be provided with a hook, for hanging within the cavity.

In accordance with a further aspect of the present invention there is provided a particulate composition comprising a dehumidifying compound, an odour-combating
5 compound, and a filler comprising starch or a starch derivative or cellulose or a cellulose derivative, in admixture.

Alternatively, and in accordance with a further aspect of
10 the present invention there is provided a particulate composition comprising a dehumidifying compound, an odour-combating compound, and a filler which acts as a thickener or gelling agent for the water inside the package, in admixture.

15

The invention will now be described by way of the following, non-limiting examples.

Example 1

20

In this example the contents of a sachet to be hung in a wardrobe were as follows:

Magnesium chloride in flake form (staple source)	51wt%
25 Calcium chloride in flake form (Tokuyama)	18wt%
Potato starch in powder form (Nichiden Chemical)	24.9wt%
ZEOCROS E100 (zeolite, Ineos Silicas)	5wt%
ACTICIDE NC preservative (Thor Specialties)	0.1wt%
Microencapsulated fragrance	1.0wt%

30

These materials were mixed in a tumbler mixer. 55g portions were sandwiched between two rectangular sheets of plastics materials, heat sealed together around their

edges, one sheet being polyethylene impermeable to water and water vapour and the other being of semi-permeable TYVEK membrane material from Du Pont, formed from fine HDPE fibres. The water-vapour permeability in this
5 embodiment is about 2000-4000g/m²/day.

A plastics hook was adhered to the package to enable it to be hung inside a wardrobe.

10 When the sachet approaches saturation the contents become gel-like. This condition is easy to detect manually.

In a similar example 27g portions of the same material were employed, between smaller sheets of the same plastics
15 materials. These smaller packages are for use in drawers.

Example 2

In this example the contents of a pouch to be placed
20 inside a shoe were as follows:

Magnesium chloride in flake form (staple source)	40wt%
Potato starch in powder form (Nichiden Chemical)	38.9wt%
Sodium bicarbonate (staple source)	10wt%
25 ZEOCROS E100 (zeolite, Ineos Silicas)	10wt%
ACTICIDE NC (Thor Specialties)	0.1wt%

These materials were mixed in a tumbler mixer. 100g portions were entrapped between two rectangular sheets of
30 plastics material, heat sealed together around their edges, one sheet being of polypropylene impermeable to liquid water and water vapour and the other being semi-permeable TYVEK membrane material. The water vapour

permeability in this embodiment is about 2000-4000g/m²/day.

In use, the pouch is placed in a shoe which is damp from wear and/or which requires storage. When approaching saturation the contents became gel-like, easily detected by feel.

ZEOCROS E100, ACTICIDE NC and TYVEK are believed to be trade marks.

Claims

1. A method of absorbing water vapour and of combating
malodour within a cavity, the method comprising the
5 step of introducing into the cavity a package
comprising a wall material which retains particulate
contents and is permeable to water vapour, the
contents comprising a dehumidifying compound, an
odour-combating compound, and a filler comprising
10 starch or a starch derivative or cellulose or a
cellulose derivative.
2. A method of absorbing water vapour and of combating
malodour within a cavity, the method comprising the
15 step of introducing into the cavity a package
comprising a wall material which retains particulate
contents and is permeable to water vapour, the
contents comprising a dehumidifying compound, an
odour-combating compound, and a filler which acts as a
20 thickener or gelling agent for the water inside the
package.
3. A method as claimed in claim 1 or 2, wherein the
contents further comprise a filler which is an
25 alkaline compound able to neutralise foot acids.
4. A method as claimed in claim 3, wherein said alkaline
compound is sodium bicarbonate.
- 30 5. A method as claimed in any preceding claim, wherein
the dehumidifying compound is capable of absorbing at
least its own weight of moisture.

6. A method as claimed in any preceding claim, wherein the dehumidifying compound is a water absorbing metal salt or oxide.
- 5 7. A method as claimed in claim 6, wherein the dehumidifying compound is selected from calcium chloride and magnesium chloride.
- 10 8. A method as claimed in any preceding claim, wherein the dehumidifying compound is present in an amount of at least 10wt% of the weight of the dry contents.
- 15 9. A method as claimed in any preceding claim, wherein the dehumidifying compound is present in an amount of no more than 95wt% of the weight of the dry contents.
10. A method as claimed in any preceding claim, wherein the odour-combating compound is a zeolite.
- 20 11. A method as claimed in any preceding claim, wherein the odour-combating compound is present in an amount at least 0.5wt% of the weight of the dry contents.
- 25 12. A method as claimed in any preceding claim, wherein the odour-combating compound is present in an amount of no more than 25wt% of the weight of the dry contents.
- 30 13. A method as claimed in claim 1 or 2, wherein the filler comprises starch or a starch derivative.

14. A method as claimed in any preceding claim, wherein the filler constitutes at least 10wt% of the weight of the dry contents.
- 5 15. A method as claimed in any preceding claim, wherein the filler constitutes no more than 80wt% of the weight of the dry contents.
- 10 16. A method as claimed in any preceding claim, wherein the contents further comprise a fragrance.
17. A method as claimed in any preceding claim, wherein the cavity is the interior of an article of footwear or a storage space within an article of furniture.
- 15 18. A package comprising a wall material which retains particulate contents and is permeable to water vapour, the contents comprising a dehumidifying compound, an odour-combating compound and a filler comprising starch or a starch derivative or cellulose or a cellulose derivative, in admixture.
- 20 19. A package comprising a wall material which retains particulate contents and is permeable to water vapour, the contents comprising a dehumidifying compound, an odour-combating compound and a filler which acts as a thickener or gelling agent for the water inside the package, in admixture.
- 25 20. A particulate composition comprising a dehumidifying compound, an odour-combating compound, and a filler comprising starch or a starch derivative or cellulose or a cellulose derivative, in admixture.
- 30

21. A particulate composition comprising a dehumidifying compound, an odour-combating compound, and a filler which acts as a thickener or gelling agent for the water inside the package, in admixture.

22. A method of absorbing water vapour and combating malodour within a cavity, or a package or particulate composition for the same purpose, substantially as described herein.

INTERNATIONAL SEARCH REPORT

Internat Application No

PCT/GB 03/00352

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 A61L9/01 A61L9/012 A61L9/014 B01D53/14 B01D53/26
B01D53/28 B01J20/04 B01J20/10 B01J20/18 B01J20/24

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 A61L B01D B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

WPI Data, PAJ, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Section Ch, Week 198645 Derwent Publications Ltd., London, GB; Class A97, AN 1986-295021 XP002241652 & JP 61 216715 A (SHIN NISSO KAKO CO LTD), 26 September 1986 (1986-09-26)	1,2,5-7, 10,13, 18-21
Y	abstract	3,4,8,9, 11,12, 14-17



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *G* document member of the same patent family

Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

Int Application No
PCT/GB 03/00352

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>DATABASE WPI Section Ch, Week 199339 Derwent Publications Ltd., London, GB; Class A97, AN 1993-308422 XP002241653 & JP 05 220327 A (DAI-ICHI TECHNOS KK), 31 August 1993 (1993-08-31) abstract</p> <p>----</p>	<p>1,2,5-7, 10,13, 18-21</p>
X	<p>DATABASE WPI Section Ch, Week 198548 Derwent Publications Ltd., London, GB; Class A97, AN 1985-299486 XP002241654 & JP 60 206425 A (ENKLAR BUSINESS KK), 18 October 1985 (1985-10-18) abstract</p> <p>----</p>	<p>1,2,5-7, 10,13, 18-21</p>
Y	<p>DATABASE WPI Section Ch, Week 199601 Derwent Publications Ltd., London, GB; Class A97, AN 1996-008643 XP002241655 & KR 9 402 336 B (HONG C), 23 March 1994 (1994-03-23) abstract</p> <p>----</p>	<p>8,9,11, 12,14,15</p>
Y	<p>EP 1 157 672 A (PROCTER & GAMBLE) 28 November 2001 (2001-11-28) paragraphs '0002!', '0007!', '0014!', '0033!'-'0040!</p> <p>----</p>	<p>3,4,16, 17</p>
A	<p>DATABASE WPI Section Ch, Week 199028 Derwent Publications Ltd., London, GB; Class J01, AN 1990-213833 XP002241656 & JP 02 144121 A (SHIN TOHOKU KOGYO), 1 June 1990 (1990-06-01) abstract</p> <p>----</p>	<p>1,2,7, 10,18-21</p>
A	<p>EP 0 832 686 A (UNITED CATALYSTS INC) 1 April 1998 (1998-04-01) column 1, line 5-10 column 1, line 38 -column 2, line 30 column 2, line 43 -column 3, line 5 column 3, line 16 -column 3, line 27; figure 1</p> <p>-----</p>	<p>1,2, 18-21</p>

INTERNATIONAL SEARCH REPORT

International application No.
PCT/GB 03/00352

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 22
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this International application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

Continuation of Box I.2

Claims Nos.: 22

Present claim 22 relates to an extremely large number of possible methods. In fact, the claim contains so many options, variables, and possible permutations that a lack of clarity within the meaning of Article 6 PCT arises to such an extent as to render a meaningful search of the claims impossible. Consequently, the search has been carried out for those parts of the application which do appear to be clear (and/or concise), namely claims 1-21.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

Int Application No
PCT/GB 03/00352

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